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CO-PROCESSING OF COAL AND SHALE OIL

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By using shale oil as a vehicle oil in coal liquefaction, low hydrogen consumption, low yield of gaseous products, a high yield of hexane-soluble fraction and high conversion of coal were brought about. Hexane-soluble fraction rich in hydrogen was obtained. The oxygen and nitrogen contents of hexane-soluble fraction were lower than in the original shale oil.

Energy demands for various uses and feedstocks in the petrochemical industry will be met in part in near future with non-petroleum sources because of the shortage and the high prices of petroleum. Coal, shale oil and tar sand bitumen are promising sources of long-range supplies of alternatives to petroleum. In countries producing both coal and shale oil such as the U.S.A., Australia and China, the co-processing of coal and shale oil will be advantageous.

In the present paper, the co-processing of Wandoan coal from Australia and shale oil from Condor, Australia was studied.

The analytical data of shale oil from Condor, Australia and anthracene oil derived from coal were shown in Table 1. Shale oil from Condor, Australia was kindly supplied by Japan Oil Shale Engineering Ltd. The results of liquefaction of Wandoan coal (C: 72.7 %, H: 5.8 %, N: 1.0 %, O: 20.5 %) from Australia by using shale oil and anthracene oil as vehicle oil were shown in Table 2. In the experiments of coal liquefaction, 10g of dry Wandoan coal, 1g of dry red-mud catalyst, 0.1g of sulfur as promoter and 15g of vehicle oil were charged in a shaking type of 500ml autoclave. Initial pressure of hydrogen was adjusted to reach 220-230 kg/cm^2 of reaction pressure. Reaction temperature was 400 °C or 450 °C. The heating rate to reaction temperature was 4 °C/min. Of the reaction products, liquid and solid products were extracted with hexane and toluene successively, which resulted in 3 fractions : hexane-soluble fraction, hexane-insoluble/toluene-soluble fraction (asphaltene) and organic toluene insolubles (unreacted coal). Coal conversion was calculated on the basis of unreacted coal. In the results in Table 2 corrections are made on the results of anthracene oil or shale oil alone, and the results become on the moisture- and ash-free coal basis.

Both coal conversions in the presence of shale oil or anthracene oil as the vehicle oil are almost equal at 400 °C and 450 °C, respectively; 73-88 wt% at 400 °C and 90-93 wt% at 450 °C. However, at 450 °C in the presence of shale oil hydrogen

Table 1. Analytical data of anthracene oil and shale oil

	Ultimate analysis (wt%.d.a.f.)				Atomic ratio			Hydrogen distribution			Type analysis (wt%)				Boiling range distribution (wt%)			
	C	H	N	O	H/C	N/C	O/C	Ha	Hα	Ho	SA.[a]	AR.[b]	RE.[c]	AS.[d]	Naphtha Fr. (IBP— 200°C)	Middle Fr. (200 — 325°C)	Heavy Fr. (325 — 400°C)	Residue (400°C— FBP)
Anthracene oil	90.1	6.2	1.1	2.4	0.83	0.01	0.02	0.687	0.264	0.049	0.0	90.3	9.7	0.0	1.6	37.6	39.6	21.2
Shale oil	84.8	12.4	2.0	1.4	1.75	0.02	0.01	0.064	0.197	0.740	30.8	22.9	42.4	4.0	0.0	27.0	29.9	43.1

a) Saturates b) Aromatics c) Resin d) Asphaltene

Table 2. Results of liquefaction of Wandoan coal

Reaction temp/°C	Reaction time/min	Product distribution (wt%. d.a.f. coal basis)			Conversion	Hydrogen consumption
		Gas	Oil + Water	Asphaltene	(wt%. d.a.f. coal basis)	(wt%. d.a.f. coal basis)
				Anthracene oil		
400	16	4.64	52.49	21.70	78.83	2.43
	61	6.75	60.12	21.54	88.41	3.17
	121	7.07	63.66	16.87	87.60	4.15
450	11	11.74	75.52	3.52	90.78	4.71
	60	16.10	74.90	0.91	91.91	7.17
	117	19.39	72.25	1.42	93.06	8.10
				Shale oil		
400	20	5.26	49.57	18.68	73.51	2.77
	63	6.33	57.52	19.65	83.50	1.91
	121	8.37	64.36	13.21	85.94	4.37
450	15	8.02	79.67	3.62	91.31	3.37
	63	11.31	79.07	1.03	91.41	5.54
	123	9.64	81.50	0.51	91.65	5.60

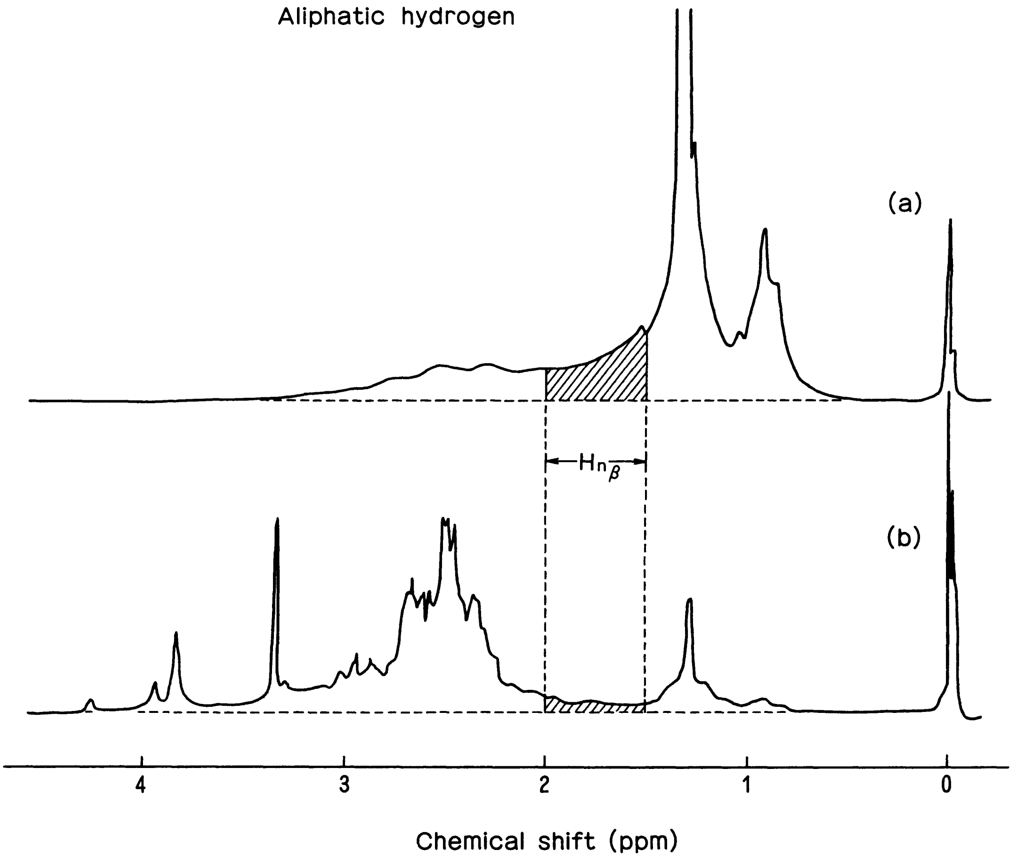

Fig. 1. Aliphatic hydrogen region of ^{1}H-NMR spectra of (a) shale oil; (b) anthracene oil.

Table 3. Analytical data of hexane-soluble fraction

Reaction temp/°C	Reaction time/min	Ultimate analysis (wt%. d.a.f.)				Atomic ratio		
		C	H	N	O	H/C	N/C	O/C
			Anthracene oil					
400	16	89.69	7.30	1.09	2.15	0.977	0.010	0.018
	61	89.01	7.23	1.17	2.44	0.975	0.011	0.021
	121	88.64	7.37	1.16	2.19	1.000	0.011	0.019
450	11	89.83	7.66	1.06	1.91	1.023	0.010	0.016
	60	89.74	7.61	1.00	1.90	1.018	0.134	0.016
	117	88.08	7.50	1.01	1.65	1.022	0.010	0.014
			Shale oil					
400	20	84.58	12.04	1.63	1.49	1.708	0.017	0.013
	63	84.56	11.91	1.64	1.45	1.690	0.017	0.013
	121	84.08	11.63	1.62	1.37	1.660	0.017	0.012
450	15	85.06	11.13	1.53	1.66	1.570	0.015	0.015
	63	85.38	11.27	1.86	0.77	1.584	0.019	0.007
	123	85.64	11.21	1.72	0.94	1.571	0.017	0.008

consumption and yield of gaseous products are lower, and the yield of hexane-soluble fraction(including produced water) is higher than when anthracene oil was used. Such behavior of shale oil can be explained by the following reasons: (1) shale oil is richer in hydrogen donor than anthracene oil (Fig. 1), (2) nitrogen compounds[1)] in shale oil have a high free radical scavenging ability[2)] and high hydrogen donor ability.[3)] Figure 1 shows an aliphatic hydrogen region of ^{1}H-NMR spectra of shale oil and anthracene oil. Hnβ, signal in the region of 1.5 to 2.0 ppm, was assigned as β-CH_2 protons in naphthenic rings and has been used as a measure of the hydrogen donor ability.[4-7)] Hnβ/H is 0.124 in shale oil and 0.011 in anthracene oil. Hnβ is 1.54 wt% in shale oil and 0.06_7 wt% in anthracene oil. Therefore, it can be considered that shale oil is richer in donatable hydrogen than anthracene oil. According to the results of hydrotreating of shale oil alone at 450 °C, the hydrogen content of hydrotreated shale oil decreases from 12.11 wt% to 10.75 wt% and the atomic ratio H/C also decreases from 1.72 to 1.53 with the increasing reaction time of 17 min to 119 min. These results clearly show that at 450 °C shale oil releases labile hydrogen by dehydrogenation.

In Table 3, analytical data of hexane-soluble fraction are shown. Hexane-soluble fraction in Table 3 is the mixture of hexane-soluble fractions from Wandoan coal and vehicle oil. In the presence of shale oil, the yield of hexane-soluble fraction produced from Wandoan coal alone is higher (Table 2) and hydrogen contents of hexane-soluble fraction produced from co-processing are higher than when anthracene oil was used (Table 3). The atomic ratio H/C of hexane-soluble fraction produced from co-processing with shale oil is 1.6 to 1.7 and higher by 1.6 to 1.7 time as large as in the presence of anthracene oil. Oxygen contents of hexane-soluble fraction produced from co-processing with shale oil at 400 °C are about 1.4 wt% and are almost equal to the value of the original shale oil shown in Table 1. At 450 °C oxygen content of hexane-soluble fraction is 0.77 to 0.94 wt% and is lower than the value of original shale oil. Both nitrogen contents of hexane-soluble fraction obtained from co-processing at 400 °C or 450 °C are about 1.6 wt% and are lower than original shale oil. These results indicate that properties of shale oil are improved from a view point of lowering in heteroatom contents.

In conclusion, we can state that shale oil is excellent as a vehicle oil for coal liquefaction because low hydrogen consumption, low yield of gaseous products, high yield of hexane-soluble fraction and high coal conversion can be realized. In addition, it is clear that co-processing, namely liquefaction of coal and upgrading of shale oil, results in lowerings of nitrogen and oxygen contents of produced hexane-soluble fraction compared with the original shale oil.

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